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**Organic geochemistry of the early Toarcian oceanic anoxic event in Hawsker  
Bottoms, Yorkshire, England**

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## Abstract

A comprehensive organic geochemical investigation of the Hawsker Bottoms outcrop section in Yorkshire, England has provided new insights about environmental conditions leading into and during the Toarcian oceanic anoxic event (T-OAE; ~183 Ma). Rock-Eval and molecular analyses demonstrate that the section is uniformly within the early oil window. Hydrogen index (HI), organic petrography, polycyclic aromatic hydrocarbon (PAH) distributions, and tricyclic terpane ratios mark a shift to a lower relative abundance of terrigenous organic matter supplied to the sampling locality during the onset of the T-OAE and across a lithological transition. Unlike other ancient intervals of anoxia and extinction, biomarker indices of planktonic community structure do not display major changes or anomalous values. Depositional environment and redox indicators support a shift towards more reducing conditions in the sediment porewaters and the development of a seasonally stratified water column during the T-OAE. In addition to carotenoid biomarkers for green sulfur bacteria (GSB), we report the first occurrence of okenane, a marker of purple sulfur bacteria (PSB), in marine samples younger than ~1.64 Ga. Based on modern observations, a planktonic source of okenane's precursor, okenone, would require extremely shallow photic zone euxinia (PZE) and a highly restricted depositional environment. However, due to coastal vertical mixing, the lack of planktonic okenone production in modern marine sulfidic environments, and building evidence of okenone production in mat-dwelling Chromatiaceae, we propose a sedimentary source of okenone as an alternative. Lastly, we report the first parallel compound-specific  $\delta^{13}\text{C}$  record in marine- and terrestrial-derived biomarkers across the T-OAE. The  $\delta^{13}\text{C}$  records of short-chain *n*-alkanes, acyclic isoprenoids, and long-chain *n*-

alkanes all encode negative carbon isotope excursions (CIEs), and together, they support an injection of isotopically light carbon that impacted both the atmospheric and marine carbon reservoirs. To date, molecular  $\delta^{13}\text{C}$  records of the T-OAE display a negative CIE that is smaller in magnitude compared to the bulk organic  $\delta^{13}\text{C}$  excursion. Although multiple mechanisms could explain this observation, our molecular, petrographic, and Rock-Eval data suggest that variable mixing of terrigenous and marine organic matter is an important factor affecting the bulk organic  $\delta^{13}\text{C}$  records of the T-OAE.

Keywords: Toarcian oceanic anoxic event; lipid biomarkers; okenane; photic zone euxinia, stable carbon isotopes; Hawsker Bottoms

## 1. Introduction

Several transient episodes of enhanced deposition and preservation of organic-rich sediments punctuated the Mesozoic Era. A combination of factors may have caused these intervals, known as oceanic anoxic events (OAEs), including greenhouse conditions and enhanced marine productivity (e.g. Schlanger and Jenkyns, 1976; Jenkyns, 1980; 1988; 2010; Trabucho-Alexandre et al., 2010). The first Mesozoic OAE was the Early Jurassic Toarcian OAE (T-OAE; ~183 Ma), which was associated with elevated extinction rates, enhanced weathering rates, warm temperatures, ocean acidification, and a negative carbon isotope excursion (CIE) (Hesselbo et al., 2000; Cohen et al., 2004; Bambach, 2006; Hesselbo et al., 2007; Jenkyns, 2010; Kiessling and Simpson, 2011). The duration of the T-OAE is not precisely known but may have lasted on the order of several hundred thousand years (Kemp et al., 2005; Suan et al., 2008; Kemp et al., 2011). The Karoo and Ferrar igneous provinces, which erupted at  $183 \pm 1$  Ma, may have coincided with the Pliensbachian-Toarcian extinction (Pálffy and Smith, 2000; Courtillot and Renne, 2003). However, better radiometric dating of the volcanism and OAE are required to confidently link these two events. Although multiple mechanisms have been proposed to account for the Toarcian negative CIE, including methane hydrate dissociation, upwelling of isotopically light waters, thermogenic release of methane, and biomass burning (Hesselbo et al., 2000; Schouten et al., 2000; McElwain et al., 2005; van de Schootbrugge et al., 2005; Finkelstein et al., 2006), the source of the isotopically light carbon remains unclear.

The analysis of sedimentary organic matter provides the opportunity to evaluate environmental and ecological responses to carbon cycle perturbations, as well as potentially constraining the perturbation itself. Previous organic geochemical work across the T-OAE has indicated changes in planktonic community structure and redox chemistry, particularly the development of photic zone euxinia (PZE) (e.g. Farrimond et al., 1989; 1994; Schouten et al., 2000; Pancost et al., 2004; Schwark and Frimmel, 2004; Bowden et al., 2006; van Breugel et al., 2006). However, since biomarker records can reflect local responses, additional comprehensive organic geochemical studies from multiple locations are required to build a global perspective of ecological and environmental change associated with the T-OAE. Here, we investigate the temporal variation of lipid biomarkers, Rock-Eval data, organic petrography, and compound-specific carbon isotopes from the Lower Jurassic section at Hawsker Bottoms, Yorkshire, England.

## **2. Geologic Setting and Site Description of Hawsker Bottoms, Yorkshire, England**

A well-studied section of the Toarcian OAE is located on the Yorkshire coast in northern England. We analyzed sample splits spanning 14 m of an organic-rich, lower Jurassic outcrop section in the Cleveland Basin at Hawsker Bottoms previously studied by Hesselbo et al. (2000). The lithology is dominated by black shales containing discrete levels of calcite concretions and constitutes the Jet Rock *sensu stricto* (Hesselbo and Jenkyns, 1995). The sections around Hawsker Bottoms have been used for defining the ammonite biostratigraphy of the Toarcian (Howarth, 1992).

93           The Early Jurassic paleogeography of the area, although somewhat uncertain, is  
94 depicted in published paleogeographic maps (e.g. Bradshaw et al., 1992). The Cleveland  
95 Basin of North Yorkshire was part of a system of shallow epicontinental seas and small  
96 extensional tectonic basins linked to the Central Graben via the Sole Pit Basin. The  
97 region formed part of the broad epicontinental sea that covered much of northwest  
98 Europe. Marine sedimentation was initiated during the Late Triassic, and a succession of  
99 marine siliciclastic mudstones accumulated during the Early Jurassic.

100           The Grey Shale Member of the Whitby Mudstone Formation consists of  
101 bioturbated, silty mudstones with beds of calcareous siderite concretions. The mudstones  
102 have thin sharp-based beds, wave ripple, and starved ripple laminations (Wignall et al.,  
103 2005; Ghadeer and Macquaker, 2011). Grain size and bioturbation intensity decrease  
104 toward the top of the unit, and sediment color darkens. The Jet Rock Member consists of  
105 dark, organic matter-rich, fissile mudstones with abundant ammonites and horizons of  
106 calcareous nodules. The boundary between these two members of the Whitby Mudstone  
107 Formation likely represents an increase in water depth in the basin.

108           The early Toarcian (*D. tenuicostatum* Zone) was a period of major basin  
109 subsidence throughout England. Organic matter content fluctuates through the Grey  
110 Shales, but increasing levels of organic matter are present from the *D. semicelatum*  
111 Subzone to the *C. exaratum* Subzone (*H. falciferum* Zone). Minor shoaling cycles with  
112 striped siltstone laminae suggest that water depths were on the order of tens of meters  
113 (Powell, 2010). Similarly, sedimentary structures suggest deposition during storms by the  
114 effects of waves (Wignall et al., 2005; Ghadeer and Macquaker, 2011). Thus, bottom  
115 water conditions were more energetic than is commonly thought, where the water column

was likely shallower than 50 m. Consequently, Hawsker Bottoms likely represents an inner continental shelf environment, which physical oceanographers define as the region where turbulence from the surface and bottom boundary layers effectively homogenizes the whole water column (Lentz and Fewings, 2012). Accordingly, inner shelf environments are typically a few meters to tens of meters deep

The abundance of ammonites in the shales indicates that the water column was at times oxygenated and favorable to nektonic faunas (Powell, 2010). The abundance of thin beds with tops homogenized by bioturbation suggests that long-term, persistent bottom water anoxia did not occur in the basin (Ghadeer and Macquaker, 2011). Besides deposition as bedload by geostrophic flows and density currents, additional sediment was supplied by suspension settling. Textural analyses have shown that much of the sedimentary organic matter was delivered to the seafloor as fecal pellets, flocs, or other organo-mineralic aggregates (Ghadeer and Macquaker, 2011). The contribution of a biogenic component to rock composition varies, and the differences have been attributed to a changing balance of primary production relative to dilution and length of transport path during deposition (Macquaker and Taylor, 1996; Wignall et al., 2005; Ghadeer and Macquaker, 2011).

### **3. Methods**

Powdered rock samples were analyzed by Rock-Eval pyrolysis. The total organic carbon (TOC; %),  $T_{\max}$  (°C),  $S_1$ , and  $S_2$  were determined and used to calculate the hydrogen index (HI) and production index (PI). Kerogen isolates from four samples across the section were mounted onto slides in duplicate and assessed optically under



white light and fluorescent light using a Zeiss research microscope and a Zeiss x 40 Plank-Neofluar objective. A Zeiss Axioskop, Axio Image D1, and a Zeiss 18 filter set were used to take photomicrographs and fluorescence images.

Powdered samples (~ 5 g) were extracted using a Dionex ASE 200 Accelerated Solvent Extractor with a solvent mixture of dichloromethane:methanol 9:1 (v/v). Elemental sulfur was removed from the total lipid extract (TLE). Asphaltenes were separated from the maltene fraction, which was then separated into saturated, aromatic, and polar fractions by silica gel chromatography. The saturated and aromatic fractions were analyzed by gas chromatography-mass spectrometry (GC-MS) and gas chromatography-metastable reaction monitoring-mass spectrometry (GC-MRM-MS). Carbon isotopic measurements of saturated hydrocarbons were made by gas chromatography/combustion/ isotope ratio mass spectrometry (GC-C-IRMS) using a ThermoFinnigan Delta Plus XP coupled to a ThermoFinnigan Trace GC. The mean value of triplicate analyses are reported here in per mil (‰) relative to Vienna Pee Dee belemnite (VPDB), and the standard deviation from the mean value was 0.4‰ or less. A detailed description of methods is included in the supplementary online material (SOM).

## **4. Results and Discussion**

### *4.1 Rock-Eval analysis*

Rock-Eval results provided insight into the thermal maturity and type of organic matter preserved in the Hawsker Bottoms sediments. The TOC percentage (Hesselbo et al., 2000) was plotted for comparison with the HI, PI, and  $T_{\max}$  (fig. 1). The narrow range of the PI (0.11-0.18) and  $T_{\max}$  (429-440°C) parameters indicate that thermal maturity is

uniform through the section and at the early stage of oil generation (Peters et al., 2005).  
Molecular indices of thermal maturity further substantiate this conclusion (see section  
4.2).

The HI data reveal that the type of organic matter undergoes a transition that  
appears to coincide with a lithological transition from medium grey shale to dark grey  
thin-bedded shale within the limitations of our sampling resolution. The low HI values  
below -2.5 m are characteristic of type III kerogen, whereas the higher HI values above -  
3 m are characteristic of type II kerogen (Peters et al., 2005). Type III kerogen is  
dominated by either terrigenous or highly degraded organic matter, and type II kerogen is  
typically derived from marine organic matter (Peters et al., 2005).

Published HI values from other T-OAE localities also increase across the  
initiation of the CIE (Prauss et al., 1991; Schouten et al., 2000; Röhl et al., 2001;  
Sabatino et al., 2009; Suan et al., 2011). Previous workers have attributed the HI  
variability to different degrees of organic matter degradation under varying redox  
conditions (Schouten et al., 2000; Röhl et al., 2001; Sabatino et al., 2009). Alternatively,  
others have argued that the HI variability represents a shift in the composition of the  
organic matter (Suan et al., 2011). Petrographic and molecular evidence for the presence  
of plant-derived material in these sediments (see section 4.3) supports the conclusion that  
lower HI values at the bottom of the section are due to a larger abundance of terrigenous  
organic matter relative to marine organic matter.

#### *4.2 Molecular indicators of thermal maturity*

The thermal history of the section was further assessed according to molecular thermal maturity parameters (fig. 2). The C<sub>31</sub> hopane 22S/(22S+22R) ratio was constant through the section and exhibited a narrow range between 0.58 and 0.59. A value of ~0.55 represents the endpoint which is reached around the main phase of oil generation (Peters et al., 2005). The C<sub>30</sub> hopane  $\beta\alpha/(\beta\alpha+\alpha\beta)$  ratio ranged from 0.08 to 0.11, which is close to values indicative of a mature source rock (Peters et al., 2005). The C<sub>29</sub> sterane  $\alpha\alpha\alpha$  20S/(20S+20R) ratio varied from 0.52 to 0.57, which is comparable to the endpoint value of 0.52-0.55 (Peters et al., 2005). In summary, molecular thermal maturity indicators corroborate the Rock-Eval results, further supporting a uniform thermal maturity within the early window of oil generation.

Some biomarker-based thermal maturity parameters can be influenced by additional factors such as source and diagenetic effects (Moldowan et al., 1986; Dahl et al., 1993; Peters et al., 2005; Bennett and Olsen, 2007; French et al., 2012). Indeed, two of the thermal maturity parameters presented in figure 2 exhibit some variation tracking changes in lithology and source input, despite the multiple lines of evidence supporting constant thermal maturity through the section. The Ts/(Ts+Tm) ratio, where Tm is C<sub>27</sub> 17  $\alpha$ -trisnorhopane and Ts is C<sub>27</sub> 18  $\alpha$ -trisnorhopane, varied from 0.41 to 0.59, whereas the diasterane/sterane ratio of C<sub>27-29</sub> compounds ranged from 1.08 to 1.44. Both ratios deviate from a relatively constant pattern in the lower ~2 meters of the section. This pattern is explained by changes in lithology and/or organic matter source input, which is consistent with lower HI values and additional evidence supporting variable terrigenous organic input (see section 4.3).

#### 4.3 Biomarker and petrographic evidence of terrigenous organic matter input

A combination of molecular and petrographic analyses was performed to evaluate the relative contribution of terrigenous organic matter through the sampling interval (fig. 3). Previous work has suggested a terrigenous source for C<sub>19</sub> and C<sub>20</sub> tricyclic terpanes, which has led to the use of C<sub>19</sub>/C<sub>23</sub> and C<sub>20</sub>/C<sub>23</sub> tricyclic terpane ratios to identify input of terrigenous organic matter (Noble et al., 1986; Peters et al., 2005). These two ratios display higher values in the lowest part of the section and decrease after the lithological transition at -2.5 meters, indicating relatively greater terrigenous organic matter input in the lowermost part of the sampling interval.

A wide range of PAHs was detected in the Hawsker Bottoms samples, including phenanthrene, fluoranthene, pyrene, benzo[a]anthracene, triphenylene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[e]pyrene, indeno[c,d]pyrene, dibenzo[a,h]anthracene, benzo[g,h,i]perylene, coronene, and retene. PAHs are a diverse set of compounds with multiple documented sources including products of pyrolysis, combustion, hydrothermal activity, and igneous intrusion as well as direct inputs from algae, fungi, vascular plants, and extraterrestrial organics (Kawka and Simoneit, 1990; George, 1992; Jiang et al., 2000; Sephton et al., 2005; Grice et al., 2007; Marynowski and Simoneit, 2009). PAHs have been used to reconstruct the history of wildfires, higher plant input, and anthropogenic activity, where peri-condensed, unsubstituted PAHs are markers for combustion of organic matter (Hites et al., 1977; Venkatesan and Dahl, 1989; Killops and Massoud, 1992; Kruege et al., 1994; Jiang et al., 1998; Arinobu et al., 1999; Finkelstein et al., 2005; Peters et al., 2005; Marynowski and Simoneit, 2009). Some sedimentary PAHs, such as phenanthrene, chrysene, and triphenylene, are more affected

by diagenesis or additional sources (Jiang et al., 1998; Grice et al., 2007), so they were not included in the total PAH sum plotted in figure 3b. Although the patterns are not identical, enhanced concentrations of total PAH co-occur with elevated  $C_{19}/C_{23}$  and  $C_{20}/C_{23}$  tricyclic terpane ratios in the bottom 2 meters of the sampling interval. Some PAHS, such as retene, are thought to derive from higher plants, in particular coniferous resin (Wakeham et al., 1980; Ellis et al., 1996; Jiang et al., 1998; Grice et al., 2005; Peters et al., 2005), although algal and bacterial sources have been reported as well (Wen et al., 2000). Retene was detected in all samples, and its concentration was plotted separately as a marker of higher plant input in figure 3c. Retene was more abundant in the lowest interval of the section, which is consistent with the total PAHs, tricyclic terpane ratios, and HI data.

Microscopic analysis of four kerogen samples adds an additional line of evidence supporting stratigraphic variations in kerogen type and organic matter sources. According to the petrographic results, the kerogen is comprised of as much as 80% of terrigenous organic matter in the bottom of the section and about 25-40% in the remainder of the sampling interval (fig. 3d). Since the elemental, molecular, and isotopic composition of organic matter from higher plants is distinct from marine organic matter, HI can reflect the compositional difference of distinct types of organic matter (e.g. Talbot and Livingstone, 1989). Assuming constant HI values for terrigenous and marine organic matter end-members, the percent terrigenous organic matter was estimated through the section using the linear relationship between the percent terrigenous macerals measured by optical microscopy and the corresponding HI (see SOM for more details). Calculated

values of  $f_{Terr\ OM}$  ranged from 12 to 85%, where the highest values were found in the lowermost part of the section (fig. 3e).

The stratigraphic change in the relative supply of terrigenous organic matter , which is supported by the HI, molecular, and petrographic results, may have been driven by effects related to rising sea level (Hesselbo, 2008; Suan et al., 2011). Considering that increased rates of continental weathering across the T-OAE would have enhanced delivery of terrigenous material (Cohen et al., 2004), the opposite trend recorded in our data might be best explained by progressive remoteness from the coastline on a gently sloping shelf during sea level transgression (e.g. Macquaker et al., 2010). However, sea level related effects might not be the only factor responsible for the changing signal in relative abundance of terrigenous and marine organic matter. For example, enhanced marine export productivity and/or enhanced marine organic matter preservation could have diluted the input of terrigenous organic matter, thereby changing the relative apparent contribution.

#### *4.4 Biomarker indicators of source and community structure*

Since some compounds or compound classes are associated with a particular biological source, metabolism, or physiology, molecular distributions can be informative about changes in microbial community structure. Unlike other intervals of ocean anoxia associated with mass extinction events (e.g. Xie et al., 2005; Cao et al., 2009), algal- and bacterial-derived biomarkers indicative of community structure did not vary significantly through the CIE (fig. 4). Instead, some biomarker indices that typically reflect community structure were more affected by source input at Hawsker Bottoms.

The regular sterane/17 $\alpha$ -hopane ratio is used as an indicator of the relative contributions of eukaryote and bacterial biomass. The regular sterane/hopane ratio was calculated using regular C<sub>27-29</sub> steranes and 17 $\alpha$  C<sub>29-33</sub> hopanes. The regular sterane/17 $\alpha$ -hopane ratio exhibited low values below -2.5 m, whereas it was more elevated (>0.5) and relatively constant in the top 10 m of the section. While this offset could be interpreted as a shift from a bacterially dominated environment in the lower part of the section to a eukaryotic environment above -3 m, it is more likely that a change in the organic matter source input is driving the regular sterane/17 $\alpha$ -hopane ratio variability. As well as containing low total steroid abundances, terrigenous organic matter can deliver hopanes derived from soil bacteria, thereby lowering the regular sterane/17 $\alpha$ -hopane ratio (Peters et al., 2005; Handley et al., 2010; S  enz et al., 2011; French et al., 2012).

Similarly, small deviations are found at the bottom of the section for the C<sub>27</sub>/C<sub>27-30</sub>, C<sub>28</sub>/C<sub>27-30</sub>, and C<sub>29</sub>/C<sub>27-30</sub> sterane ratios. These ratios included regular steranes as well as diasteranes and are commonly used as indicators of the relative contribution from red algae biomass, chlorophyll-c algae, and green algae, respectively. However, they can also be affected by the delivery of C<sub>29</sub> steranes derived from land plants (Moldowan et al., 1985; Peters et al., 2005). Indeed, C<sub>29</sub> sterane was the dominant sterane in samples from the bottom of the section, where it represented nearly half of the total C<sub>27-30</sub> steranes. The C<sub>30</sub>/C<sub>27-30</sub> sterane ratio, on the other hand, which is an indicator of marine pelagophyte algae, was constant throughout the section and represented only a minor proportion of the total steranes abundance.

The 2 $\alpha$ -methylhopane index (2-MHI) has been used as an indicator of cyanobacterial input (Summons et al., 1999), although additional sources were later

reported (Rashby et al., 2007). The 3 $\beta$ -methylhopane index (3-MHI) is considered a marker for aerobic proteobacteria, including methanotrophs and acetic acid bacteria (Zundel and Rohmer, 1985; Talbot et al., 2003; Farrimond et al., 2004; Talbot and Farrimond, 2007). The 2-MHI and 3-MHI were invariant, and the 3-MHI was in the range of average Phanerozoic marine values (~1-3%) (Farrimond et al., 2004; Cao et al., 2009). Likewise, the 2-MHI also lacked elevated values. Based on elevated 2-MHI, 3-MHI, and nitrogen isotope anomalies, previous workers have reported an increased contribution of diazotrophic cyanobacteria and methanotrophic bacteria during other OAEs (e.g. Kuypers et al., 2004; Cao et al., 2009; Sepúlveda et al., 2009; Luo et al., 2011). The low and invariant contribution of these microbial groups indicates that environmental conditions suitable for their predominance did not prevail at this locality. Thus, enhanced cyanobacterial diazotrophy may not fully explain the previously reported depleted bulk organic  $\delta^{15}\text{N}$  at this location during the T-OAE (Jenkyns et al., 2001).

#### *4.5 Indicators of redox change and depositional environment*

A suite of biomarkers was used to assess changes in water column stratification and redox potential, including the gammacerane index, C<sub>35</sub> homohopane index (C<sub>35</sub> HHI), pristane/phytane (Pr/Ph) ratio, and the concentration of aromatic carotenoid derivatives (fig. 5). Although some of these parameters can also be influenced by diagenesis, source input, and thermal maturity, they display patterns consistent with a shift towards more intense reducing conditions at least in the sediment porewaters and potentially in the overlying water column.



320           Although the biological sources of gammacerane are not fully known (Peters et  
321 al., 2005), it is a diagenetic product of tetrahymanol, a compound found in bacteriovorous  
322 ciliates thriving at the chemocline of stratified water bodies (ten Haven et al., 1989;  
323 Sinninghe Damsté et al., 1995). Thus, the occurrence of gammacerane, expressed as the  
324 gammacerane index =  $[gammacerane / (gammacerane + 17\alpha, 21\beta \text{ } C_{30} \text{ hopane})] * 100$ , has  
325 been used to infer changes in water column stratification in ancient environments.  
326 Gammacerane was detected in all of the analyzed samples but became more prominent in  
327 those deposited during the OAE, starting at the onset of thin-bedded shales.

328           Elevated abundances of gammacerane during the T-OAE may reflect the  
329 development of seasonal water column stratification, possibly due to stronger seasonality  
330 and/or deepening of the water column. In contrast, prior to the T-OAE, seasonality may  
331 have been weaker, or the water column may have been too shallow to stratify, even  
332 during warm months, due to turbulent mixing. The development of seasonal water  
333 column stratification at Hawsker Bottoms during the T-OAE would have aided the  
334 development of water column oxygen-depletion, particularly during warm and productive  
335 months. However, gammacerane enrichments alone do not necessitate water column  
336 anoxia, particularly given the association of its precursor, tetrahymanol, with suboxic  
337 waters in the modern (Wakeham et al., 2007; 2012).

338           The  $C_{35}$  HHI and Pr/Ph ratio are recorders of depositional redox conditions in  
339 sediments. The  $C_{35}$  HHI records the degree of preservation of the extended side chain of  
340  $C_{35}$  hopanes derived from intact bacteriohopanepolyols (BHPs) (Köster et al., 1997;  
341 Peters et al., 2005). Higher  $C_{35}$  HHI values are characteristic of oxygen-depleted marine  
342 depositional environments. Pristane and phytane in ancient marine rock extracts and oils

are largely, but not exclusively, derived from the chlorophyll phytyl side chain from photoautotrophs. Redox conditions influence the diagenetic pathway of the phytyl side chain. Reducing conditions promote the conversion of phytol to phytane, and oxic conditions promote the conversion of phytol to pristane (Didyk et al., 1978; Peters et al., 2005). The C<sub>35</sub> HHI nearly doubled in samples deposited during the OAE compared to those deposited prior to the event. Values of the Pr/Ph ratio >3 recorded at the bottom of the section are suggestive of deposition of terrigenous organic matter under oxic conditions. The Pr/Ph ratio values near or below 1 during the T-OAE, together with the elevated C<sub>35</sub> HHI, suggest intensification of reducing conditions in the sediment porewaters during deposition.

Biomarkers for anaerobic phototrophic green sulfur bacteria (GSB) have been used to argue for the development of PZE during the T-OAE (Schouten et al., 2000; Pancost et al., 2004; Bowden et al., 2006) and other OAEs (e.g. Cao et al., 2009) based on the physiological requirement of co-occurring reduced sulfur species and light. We detected 2,3,6-aryl isoprenoids, isorenieratane, and chlorobactane in all samples. Unlike previous studies of the T-OAE or any Phanerozoic organic geochemical study of marine samples, trace concentrations of okenane were also identified by GC-MRM-MS in samples above -3 m, whereas it was below detection limit in samples from the lowest 2 meters of the section. Okenone, a photosynthetic pigment belonging to the PSB family Chromatiaceae, is the only known precursor of okenane (Brocks and Schaeffer, 2008). All compounds were compared with an authentic carotenoid standard and an extract from the Barney Creek Formation (BCF; fig. 6; Brocks et al., 2005). Normalizations of the C<sub>40</sub>

aromatic carotenoid derivatives against the mass of TOC and TLE reveal a similar pattern of elevated concentrations during the anoxic event compared to the pre-event baseline.

In total, all of the organic geochemical redox indicators point towards a shift towards more reducing conditions broadly corresponding with the initiation of the negative CIE. However, sedimentological features, such as starved wave and combined flow ripples, indicate that this area was an energetic, shallow inner shelf environment on the order of tens of meters and probably no deeper than 50 m, where enough oxygen was present in the water column on some timescale to sustain nektonic fauna, including ammonites, and allow for bioturbation at the sediment-water interface through the OAE (Wignall et al., 2005; Powell, 2010; Ghadeer and Macquaker, 2011). We explore different scenarios to reconcile these apparent opposing lines of evidence.

First, the geochemical and sedimentological signals recorded in the rock record are a composite of many processes occurring on different timescales. In the modern ocean, highly productive coastal and continental margin sediments and the overlying water column oscillate between oxic and anoxic conditions over different timescales (e.g. Burdige, 2007). Enhanced productivity and export of organic matter, which are important features of Mesozoic OAEs (e.g. Erba, 2004; Jenkyns, 2010), would have increased the oxygen demand in the water column and sediment porewaters during productive months. During the T-OAE, anoxic conditions may have been restricted to the sediment porewaters during seasons of low productivity, allowing bioturbation to occur when bottom waters were better oxygenated. Conversely, oxygen-deficient waters may have expanded seasonally to the water column during intervals of high productivity and enhanced stratification, as implied by the gammacerane index.

Second, the molecular, paleontological, and sedimentary indicators of redox chemistry apply to different parts of the depositional environment, diagenetic pathways, and have different sensitivities along the redox spectrum. With the exception of the GSB and PSB carotenoid markers, the geochemical parameters reported here do not require strict anoxia or euxinia in the water column. The gammacerane index pattern supports the development of seasonal stratification during the OAE, which would have promoted oxygen depletion of the water column. However, the possibility remains that even during intervals of high productivity and stratification, water column oxygen concentrations at this location were depleted but high enough to sustain organisms with physiological oxygen requirements, thereby explaining the fossil and sedimentary evidence. Additionally, the Pr/Ph ratio and C<sub>35</sub> HHI pertain primarily to sedimentary redox conditions opposed to water column redox structure. Therefore, the occurrence of intact aromatic carotenoid derivatives merits further discussion to assess water column redox chemistry.

To date, okenane has only been reported in Paleoproterozoic rock extracts and lacustrine Cenozoic extracts (Brocks et al., 2005; Zhang et al., 2011). Given the atmospheric  $pO_2$  during the Mesozoic was near present atmospheric levels (Berner, 2006), its detection in marine samples of this age requires careful interpretation. The PSB family Chromatiaceae blooms in a range of anoxic environments with light and reduced sulfur species, including stratified lakes, fjords, coastal lagoons, estuaries, and coastal microbial mats, but not all Chromatiaceae produce okenone (Brocks and Schaeffer, 2008 and references therein). Okenone-producing planktonic Chromatiaceae dwell in water columns where the chemocline is above 25 m and in 75% of the reported cases less than

12 m (Brocks and Schaeffer, 2008). Notably, all of the modern chemocline depth observations for okenone production are based on stratified lake systems. Thus, the lack of okenone in modern marine sulfidic environments presents a “no analogue problem” for ancient marine samples containing okenane that were deposited under atmospheric  $pO_2$  close to modern levels.

Transient free sulfide has been reported in the water column of intense upwelling zones, including the Arabian Sea, Namibian coast, and the Peruvian coast (e.g Dugdale et al., 1977; Brüchert et al., 2003; Naqvi et al., 2006; Schunck et al., 2013). However, these episodes are typically short lived. In contrast, sulfidic waters persist in some restricted marine basins and fjords, including the Black Sea, Cariaco Basin, Saanich Inlet, and the Framvaren and Effingham Fjords. However, these two types of marine environments (non-restricted, transiently sulfidic and restricted, permanently sulfidic) fail to represent suitable modern analogues for Hawsker Bottoms on several counts. Isorenieratene has been measured in the water column and sediments of some restricted marine basins, particularly fjords and the Black Sea (e.g. Sinninghe Damsté and Schouten, 2006), but GSB carotenoids have not been detected in transiently sulfidic upwelling systems. Furthermore, okenone has not been reported in the water column or sediments of any modern marine transiently or permanently sulfidic environment, with the exception of the upper sediments of Kyllaren fjord, a small, highly restricted basin (Smittenberg et al., 2004; Sinninghe Damsté and Schouten, 2006). Like okenone, modern planktonic marine occurrences of chlorobactene are also limited to semi-enclosed water masses that are not representative of fully marine conditions (e.g. Naeher et al. 2012). Interestingly, multiple emerging lines of evidence suggest the occurrence of a “cryptic sulfur cycle” in some

OMZs, with a potential role for photosynthetic sulfide oxidation (Canfield et al., 2010; Stewart et al., 2012). However, the presence of GSB and/or PSB and their respective carotenoids have yet to be reported in modern OMZs.

Furthermore, the physical oceanographic processes determining the degree of vertical mixing, hence stratification and redox gradient stability, are markedly different between inner shelf environments and sulfidic, silled basins, which are highly restricted and in many classic modern examples, are an order of magnitude or more deeper than estimated paleodepths of Hawsker Bottoms. Although the water column at Hawsker Bottoms became deeper with the sea level transgression across the T-OAE, the depositional environment remained relatively shallow because of its location on a gently sloping shelf (e.g. Macquaker et al., 2010). Consequently, turbulent mixing at the surface and bottom boundary layers would have prevented a stable sulfidic chemocline from developing. On the other hand, considering the limited occurrence of planktonically produced okenone in modern lakes, a planktonic source of okenone at Hawsker Bottoms would imply that, rather than an inner shelf environment, Hawsker Bottoms was a highly restricted coastal basin not reflective of fully marine conditions.

Alternatively, we argue that okenane at Hawsker Bottoms was likely derived from benthic microbial mats based on the lack of modern analogues of okenone-production in marine sulfidic environments, the dynamics of inner shelf physical mixing, and building evidence of okenone-producing, mat-dwelling Chromatiaceae (e.g. Caumette et al., 1991; Airs et al., 2001; Caumette et al., 2004; Meyer et al., 2011). Furthermore, planktonic Chlorobiaceae are not the exclusive source of isorenieratene and chlorobactene. Previous work has documented additional non-planktonic GSB sources of isorenieratene and

chlorobactene, including microbial mats (e.g. Wahlund et al., 1991; Brocks and Summons, 2003; Beatty et al., 2005; Bühring et al., 2011). Although a mixed planktonic and mat origin of the carotenoids cannot be ruled out, it is more likely that the GSB and PSB carotenoids detected in Hawsker Bottoms samples share a source. Previous studies of sedimentary structures in the Toarcian shales of Yorkshire have attributed wavy laminations to microbial mats (O'Brien, 1990), thereby further supporting a sedimentary origin of GSB and PSB carotenoid derivatives detected in Hawsker Bottoms samples. Similar wavy laminated fabrics have been reported in coeval shales in northern European T-OAE sections (Trabucho-Alexandre et al., 2012). Unfortunately, a sedimentary source of the GSB and PSB carotenoid derivatives offers little information about water column redox chemistry. However, this interpretation does not preclude the development of a suboxic, anoxic, or euxinic water column in this region on some timescale during the T-OAE. Instead, additional inorganic geochemical data is required to better assess the water column redox conditions and degree of basin restriction (Algeo and Tribovillard, 2009).

#### *4.6 Compound specific stable carbon isotopic data*

A limited number of compound specific  $\delta^{13}\text{C}$  records of the T-OAE are currently available in the literature. Here, we report the first long-chain *n*-alkane  $\delta^{13}\text{C}$  records of the T-OAE. Compound specific  $\delta^{13}\text{C}$  analyses of marine- and terrestrial-derived lipids reveal a shift towards lighter  $\delta^{13}\text{C}$  values (fig. 7). Short-chain *n*-alkanes, as well as pristane and phytane are typically used as marine indicators, whereas long-chain *n*-alkanes primarily reflect terrigenous sources. The *n*-C<sub>17</sub>, *n*-C<sub>18</sub>, and *n*-C<sub>19</sub> alkanes displayed a negative excursion of ~2–3‰, which is consistent with the ~2–4‰ negative

excursions documented in the partial  $n\text{-C}_{16-20}$  alkane records from the Toarcian Posidonienschiefer in southwest Germany (Schouten et al., 2000). Pristane and phytane encode a muted excursion ( $\sim 1.5\text{--}2\text{‰}$ ) compared to short-chain alkane records, and they also have smaller CIE magnitudes compared to the pristane and phytane isotopic records from the Toarcian Paris Basin and the Posidonienschiefer ( $\sim 3\text{--}4\text{‰}$ ) (Schouten et al., 2000; van Breugel et al., 2006). On the other hand, long-chain  $n$ -alkanes ( $n\text{-C}_{27}$ ,  $n\text{-C}_{28}$ , and  $n\text{-C}_{29}$ ), which are primarily but not exclusively derived from epicuticular waxes of vascular plants (Eglinton and Hamilton, 1967), display the largest compound specific negative CIE ( $\sim 4\text{--}5\text{‰}$ ). The molecular isotopic records appear to register the initiation of the negative CIE earlier than in the bulk organic record, and within the CIE, the compound-specific  $\delta^{13}\text{C}$  values remain fairly stable while the bulk curve becomes gradually depleted. However, these features could be due to sampling resolution differences. Higher resolution molecular isotopic records are required to better address the timing and structure of the isotopic excursion recorded in different carbon reservoirs.

The absolute magnitude of the bulk organic CIE ( $\sim 5\text{--}7\text{‰}$ ) is larger than the CIEs recorded in the molecular records from Yorkshire (this study;  $\sim 1.5\text{--}5\text{‰}$ ), the Paris Basin ( $\sim 3\text{‰}$ ; van Breugel et al., 2006), and the Posidonienschiefer ( $\sim 2\text{--}4\text{‰}$ ; Schouten et al., 2000). Identifying the reason behind the CIE magnitude offsets is critical for placing bounds on the magnitude of isotopically light carbon added into the system. Bulk organic matter is comprised of an array of molecularly and isotopically heterogeneous constituents. In addition to environmental perturbations, organic matter source mixing can contribute to bulk organic  $\delta^{13}\text{C}$  excursions (e.g. Pancost et al., 1999). The comparison of short- and long-chain  $n$ -alkane isotopic compositions demonstrates that, unlike the



modern, terrigenous organic matter is isotopically heavier than marine organic matter during the Toarcian (fig. 7), which is consistent with previous Toarcian studies (Vetö et al., 1997; Schouten et al., 2000). Multiple lines of evidence presented in section 4.3 highlight a significant transition in the terrigenous organic matter input at Hawsker Bottoms. Indeed, the bottom 2 meters of the study interval are dominated by terrigenous organic matter and are isotopically heavier than the overlying interval that is dominated by marine organic matter. Therefore, an undetermined component of the bulk organic CIE magnitude may be attributed to source mixing effects.

Additional factors could also contribute to the difference in magnitudes between bulk and molecular CIEs. For instance, it is possible that the full CIE was not captured in the molecular isotopic records due to a lower sampling resolution compared to the bulk organic  $\delta^{13}\text{C}$  records. Alternatively, water availability can modulate the magnitude of the CIE recorded in vascular leaf waxes, as has been discussed for the Paleocene Eocene Thermal Maximum (PETM; e.g. Schouten et al., 2007; Smith et al., 2007), but unlike the PETM, the ratio of angiosperms and conifers would not account for the *n*-alkane and bulk organic CIE magnitude offset because the rise of angiosperms postdates the Early Jurassic (e.g. Heimhofer et al., 2005). Additionally, thermal maturation could influence the  $\delta^{13}\text{C}$  of individual compounds, which become isotopically heavier with increasing thermal maturity (Clayton, 1991; Clayton and Bjorøy, 1994; Tang et al., 2005).

Nevertheless, while multiple mechanisms may account for the difference between molecular and bulk organic CIE magnitudes, it is significant that a negative CIE is recorded in both marine- and terrestrial-derived lipids, albeit to different degrees. The parallel isotopic change in marine and terrestrial carbon pools recorded at Hawsker

Bottoms further supports previous studies suggesting that the T-OAE was a global carbon cycle perturbation where isotopically light carbon entered the atmospheric, terrigenous, and marine carbon reservoirs (Hesselbo et al., 2000; 2007; Al-Suwaidi et al., 2010; Caruthers et al., 2011; Gröcke et al., 2011). Multiple sources of isotopically light carbon have been proposed, including methane hydrate dissociation, regional upwelling of isotopically light waters in stratified epicontinental seas, thermogenic release of methane from organic-rich strata in contact with dykes, biomass burning, or a combination of these mechanisms (Hesselbo et al., 2000; Schouten et al., 2000; McElwain et al., 2005; van de Schootbrugge et al., 2005; Finkelstein et al., 2006).

Although our study does not provide evidence in support of a specific forcing mechanism, it allows us to narrow down potential mechanisms. A deep-water source of isotopically light carbon is unlikely because of the CIE observed in land plant biomarkers. The lack of evidence for bacterial methanotrophy in our section suggests that methane hydrate dissociation did not supply appreciable methane to the sampling locality. The organic matter source transition complicates the interpretation of PAH abundances as tracers of biomass burning, so a different sampling locality without an organic matter source transition should be studied to test the biomass burning mechanism using PAHs. A cascade of mechanisms rather than a single mechanism likely initiated the T-OAE. However, our results indicate that the influence of source mixing on the bulk organic  $\delta^{13}\text{C}$  has been previously underestimated and could have potentially affected other bulk isotopic systematics such as nitrogen. Therefore, previous estimates regarding the magnitude of this global perturbation of the carbon cycle should be revisited.

## 5. Conclusions

We use a multiproxy approach based on bulk geochemistry, lipid biomarkers, and compound-specific stable isotopes to elucidate environmental and ecological changes associated with the T-OAE at Hawsker Bottoms in Yorkshire, England. Molecular indicators and Rock-Eval results suggest that thermal maturity is uniformly in the early oil generation window throughout the sampling interval. The HI data, organic petrography, PAH distribution, and tricyclic terpane ratios indicate a transition in the relative input of terrigenous vs. marine organic matter across a lithological transition. The shift to lower relative abundance of terrigenous organic matter was likely a result of sea level related effects such as coastal proximity, changes in marine organic matter preservation, and/or dilution effects from increased marine productivity.

Organic geochemical redox and depositional environment indicators point towards an overall shift towards more reducing conditions in sediment porewaters and the development of seasonal stratification during the OAE. Previous sedimentological observations require that the water column was not completely anoxic throughout the entire T-OAE, which may seem contradictory at first to the detection of GSB and PSB carotenoids. However, here we present the first occurrence of okenane, a carotenoid marker of PSB, in marine samples younger than the Paleoproterozoic (1.64 Ga). This unexpected finding challenges the interpretation of GSB and PSB carotenoids as markers of PZE in the context of Hawsker Bottoms due to inner shelf vertical mixing, the lack of modern analogues of okenone-production in marine sulfidic environments, and the emerging evidence of okenone-producing mat-dwelling Chromatiaceae. Therefore, in combination with previous reports of microbial wavy lamination in Toarcian shales of

Yorkshire and coeval shales in northern Europe, we argue that okenane, and potentially chlorobactane and isorenieratane, was most likely mat-derived at Hawsker Bottoms.

The compound-specific  $\delta^{13}\text{C}$  records of short-chain *n*-alkanes, acyclic isoprenoids, and long-chain *n*-alkanes support a carbon cycle perturbation that affected both the atmospheric and marine systems, which precludes the recycling of isotopically light  $\text{CO}_2$  from anoxic waters as the sole mechanism responsible for the T-OAE negative CIE. Notably, compound specific  $\delta^{13}\text{C}$  records of the T-OAE, including the new data presented here from Yorkshire and previous molecular data from the Paris Basin and the Posidonienschiefer, encode negative CIEs that are smaller in magnitude compared to bulk organic  $\delta^{13}\text{C}$  records. Many mechanisms could contribute to this observation, particularly variable mixing of terrigenous and marine organic matter, which is supported by the multiple lines of evidence for a transition in organic matter source. Identifying the mechanisms behind the CIE magnitude offsets is important for estimating the magnitude of isotopically light carbon injected into the surface carbon reservoirs.

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Figure Captions:

**Fig. 1. Rock-Eval Analysis.** A) Total organic carbon (TOC; %) (Hesselbo et al., 2000); B) Hydrogen index (HI; mg HC/g TOC); C) Production index (PI); D)  $T_{max}$  (°C).

**Fig. 2. Molecular Indicators of Thermal Maturity.** A) The  $C_{31}$  hopane 22S/(22S+22R) ratio; B)  $C_{30}$  hopane  $\beta\alpha/(\beta\alpha+\alpha\beta)$  ratio; C)  $C_{29}$  sterane  $\alpha\alpha\alpha$  20S/(20S+20R) ratio; D) Ts/(Ts+Tm) ratio; E) diasteranes/steranes ratio. Note the lack of variation in A, B and C across the section compared to the minor variations exhibited by D and E due to changes in source input and/or lithology.

**Fig 3. Terrigenous Organic Matter Indicators.** A) Ratios of  $C_{19}/C_{23}$  and  $C_{20}/C_{23}$  tricyclic terpanes; B) total concentration of PAHs normalized by TOC and TLE; C) concentration of retene normalized by TOC and TLE; D) measured contribution of terrigenous organic matter (OM) by petrographic analysis; E) calculated percentage of terrigenous organic matter ( $f_{Terr OM}$ ) based on linear regression ( $f_{Terr OM} (\%) = -0.279 * HI + 136$ ;  $R^2=0.90$ ) of petrographic measurements of terrigenous organic matter (Fig. 3D) and HI (Fig. 1B).

**Fig. 4. Source and Community Indicators.** A) The ratio of regular steranes/17 $\alpha$ -hopanes; B)  $C_{27}/C_{27-30}$  steranes; C)  $C_{28}/C_{27-30}$  steranes; D)  $C_{29}/C_{27-30}$  steranes; E) 2 $\alpha$ -methylhopane and 3 $\beta$ -methylhopane indices.

**Fig. 5. Redox and Depositional Environmental Indicators.** A) Gammacerane index; B)  $C_{35}$  homohopane index ( $C_{35}HHI$ ); C) pristane/phytane (Pr/Ph) ratio; D) concentration of isorenieratane; E) concentration of chlorobactane; F) concentration of okenane. The concentrations of  $C_{40}$  carotenoids are semi-quantitative and were normalized against TOC and TLE.

**Fig. 6 Gas chromatography - metastable reaction monitoring - mass spectrometry (GC-MRM-MS) chromatogram for the identification of aromatic carotenoid derivatives.** MRM chromatograms displaying the 554→134 transition characteristic for chlorobactane and okenane in an authentic standard of combined  $C_{40}$  carotenoids (A) and in sample ENR004 at 5.98 m (C). Plots B and D are MRM chromatograms displaying the 546→134 MRM transition characteristic of isorenieratane, renieratane, and renierapurpurane in an authentic standard of combined  $C_{40}$  carotenoid (B) and in sample ENR004 (D). Compound abbreviations were used for labels: chlorobactane (Ch); okenane (Ok); isorenieratane (Iso); renieratane (Ren); renierapurpurane (Rpurp).

**Fig. 7 Carbon Isotopic records.** A) Previously reported  $\delta^{13}\text{C}_{\text{org}}$  from Hawsker Bottoms (Hesselbo et al., 2000; Kemp et al., 2005); B)  $\delta^{13}\text{C}$  of n-C<sub>17-19</sub> short-chain n-alkanes; C)  $\delta^{13}\text{C}$  of pristane and phytane; D)  $\delta^{13}\text{C}$  of n-C<sub>27-29</sub> long-chain n-alkanes. Note the different x-axis scales.

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Figure 1

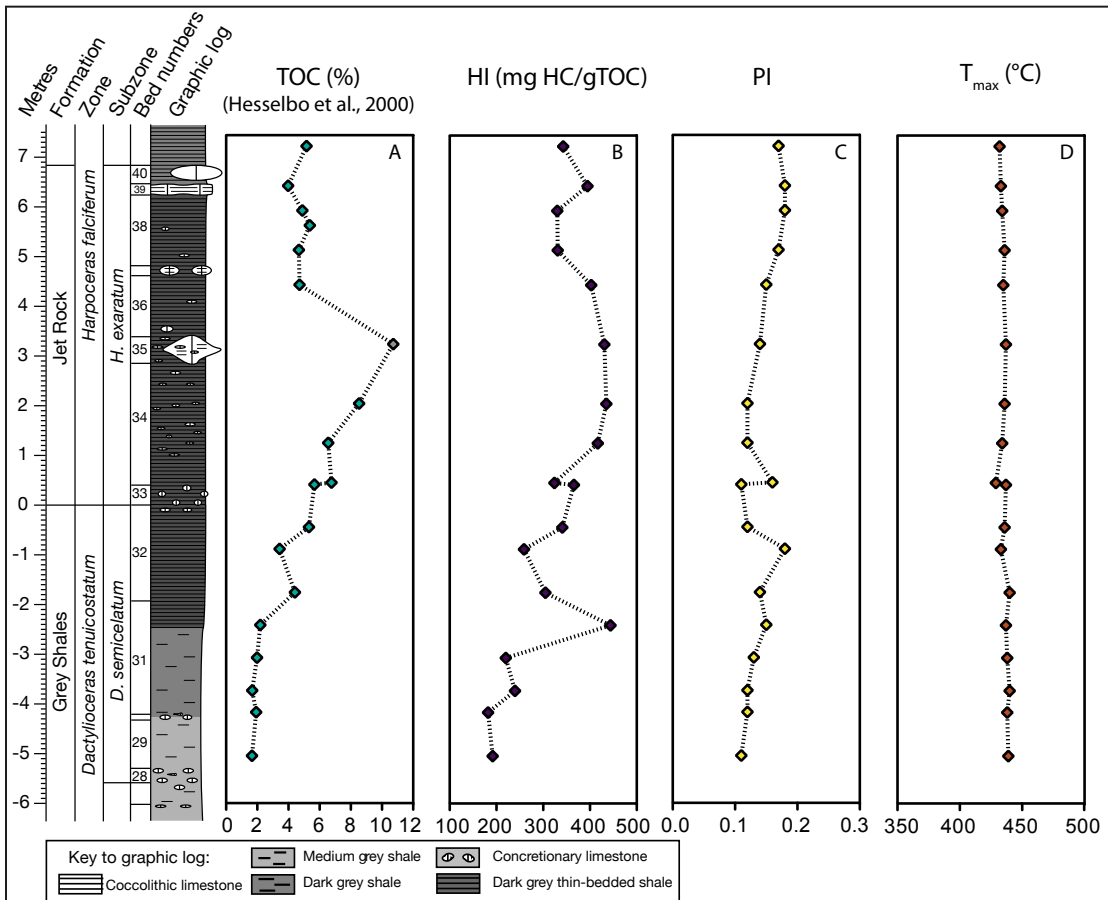


Figure 2

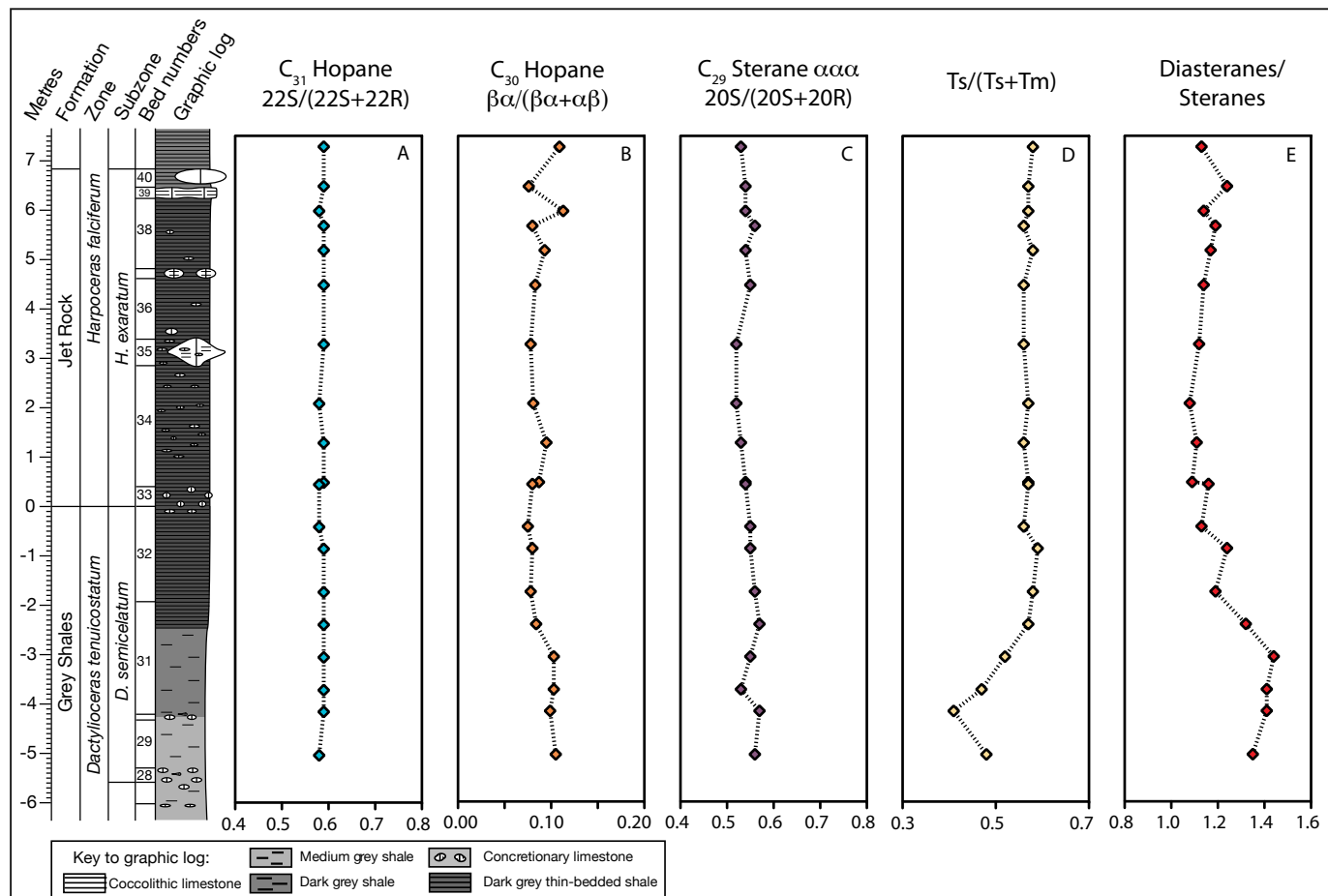




Figure 3

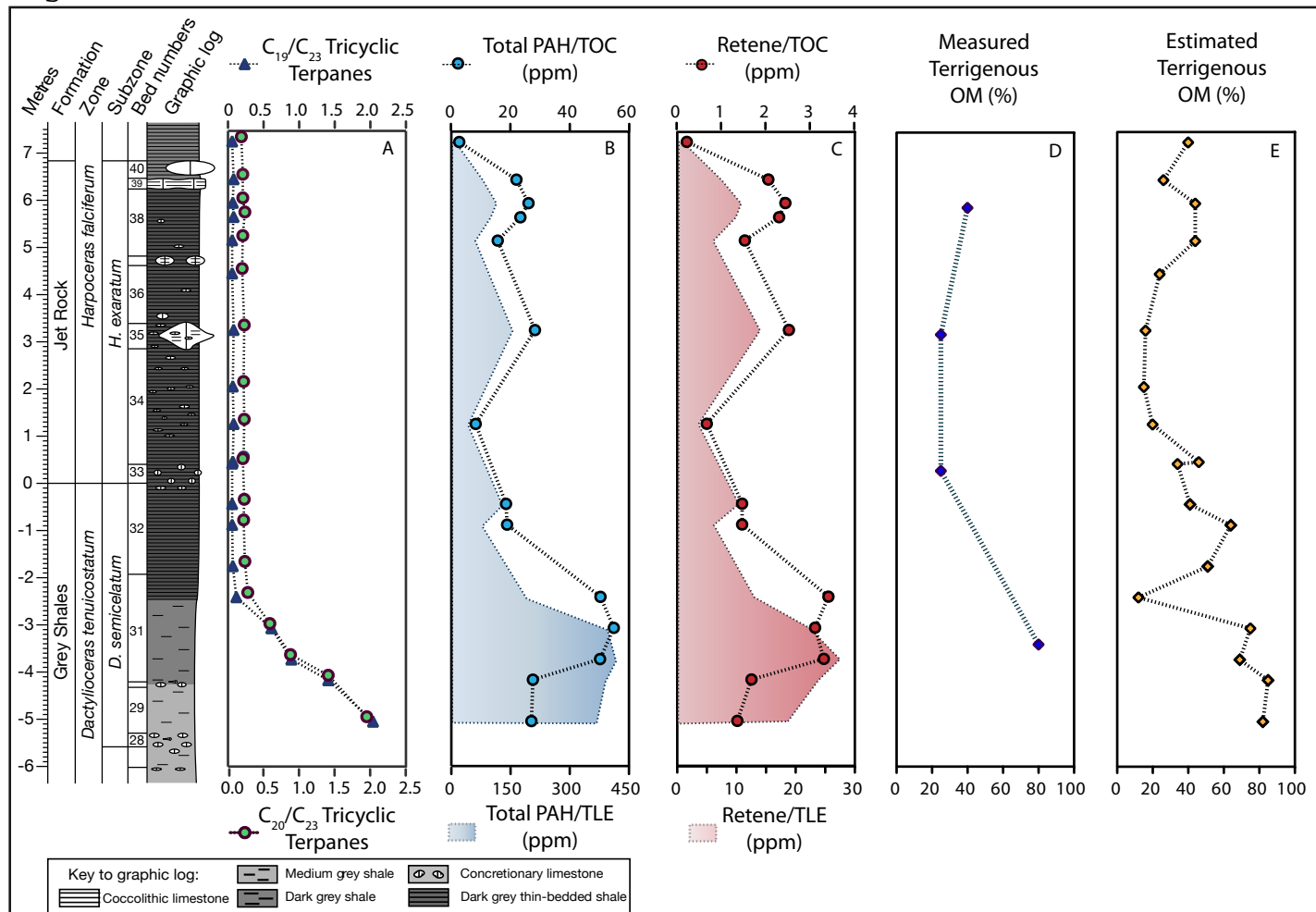


Figure 4

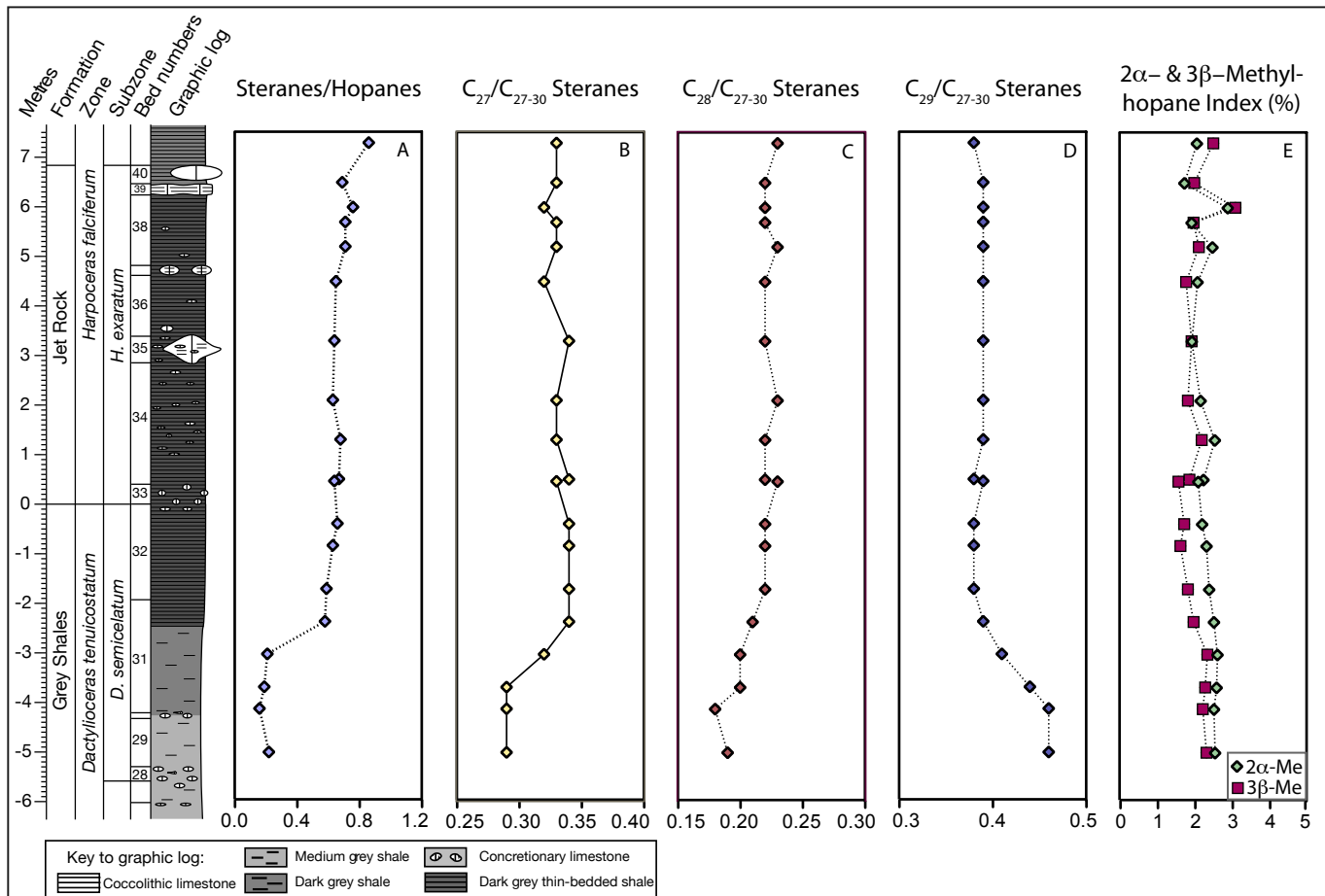


Figure 5

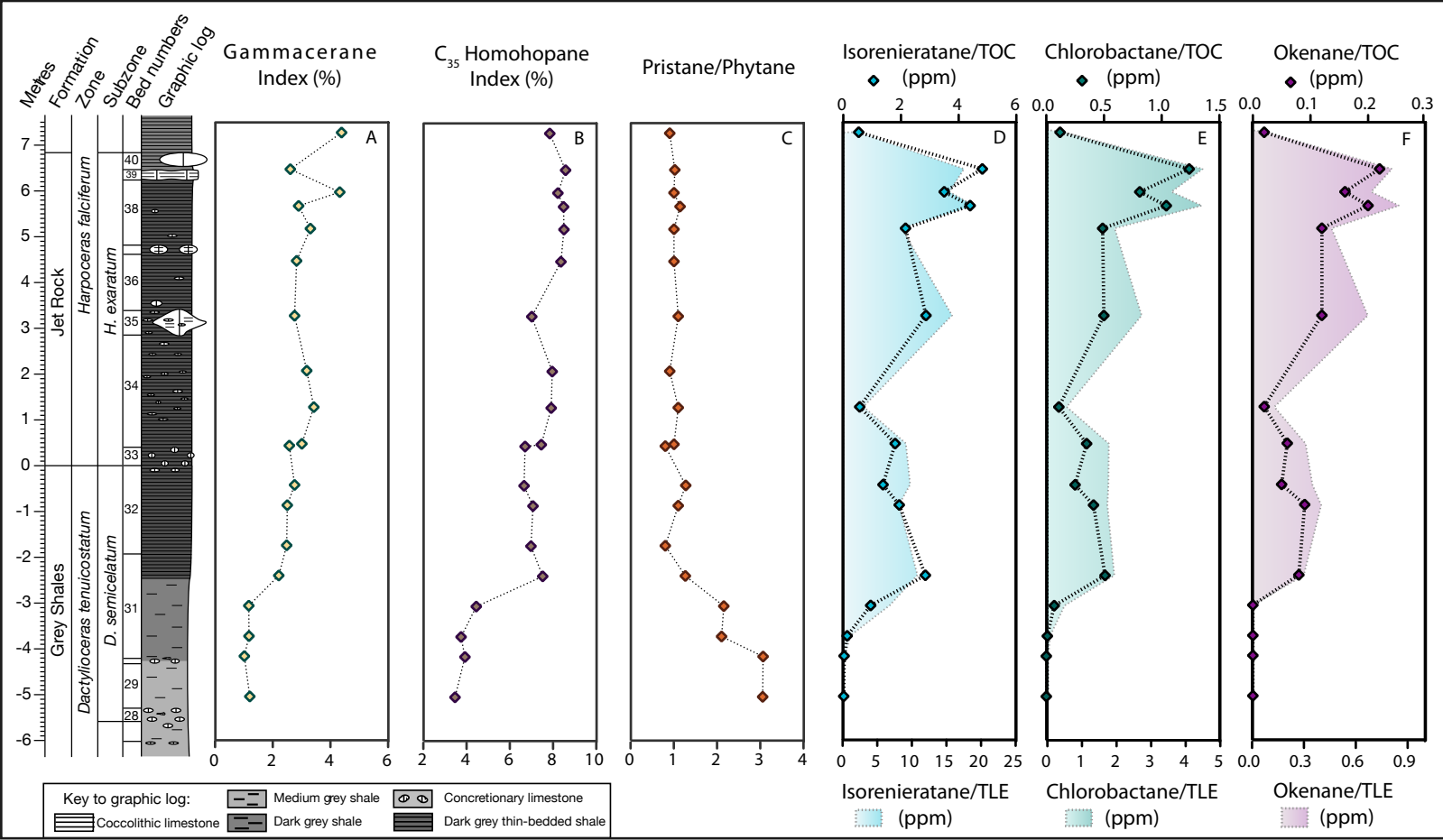


Figure 6

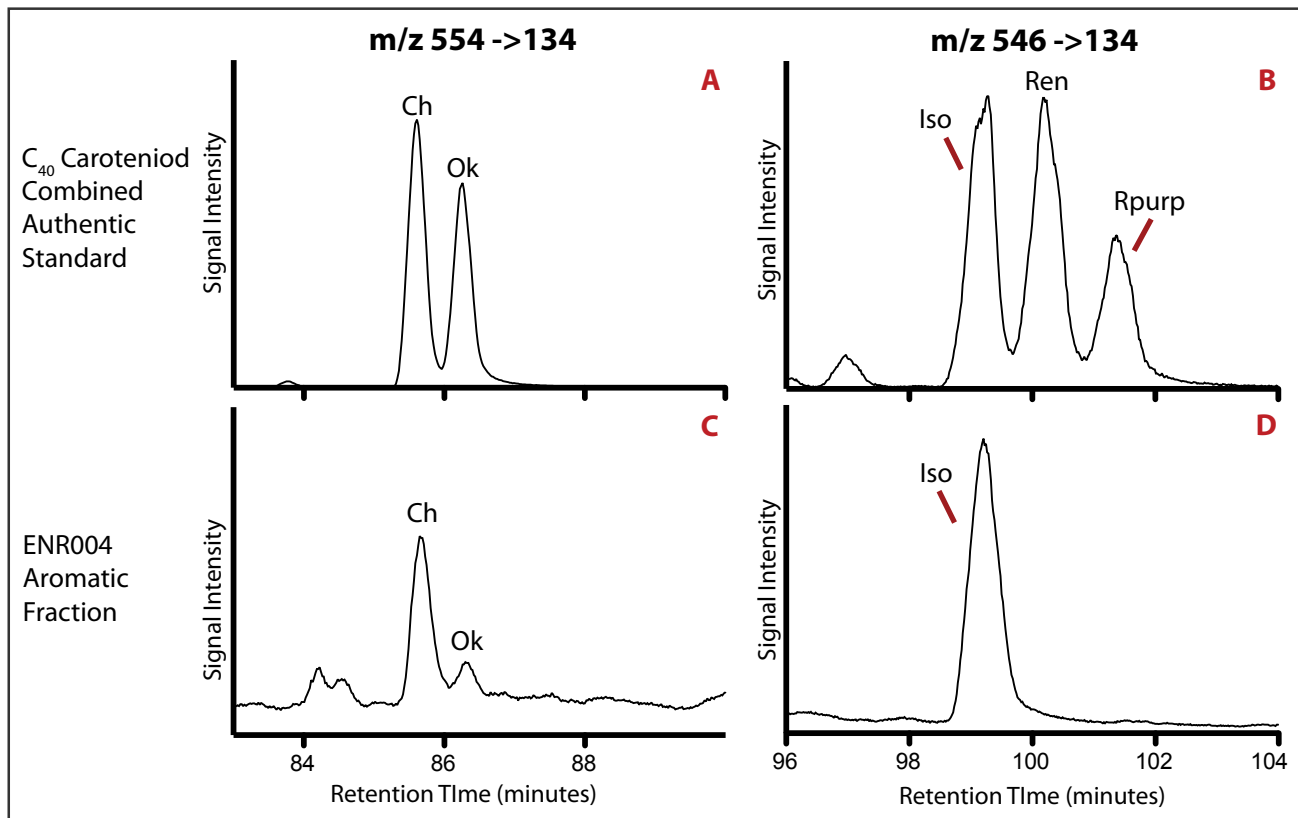
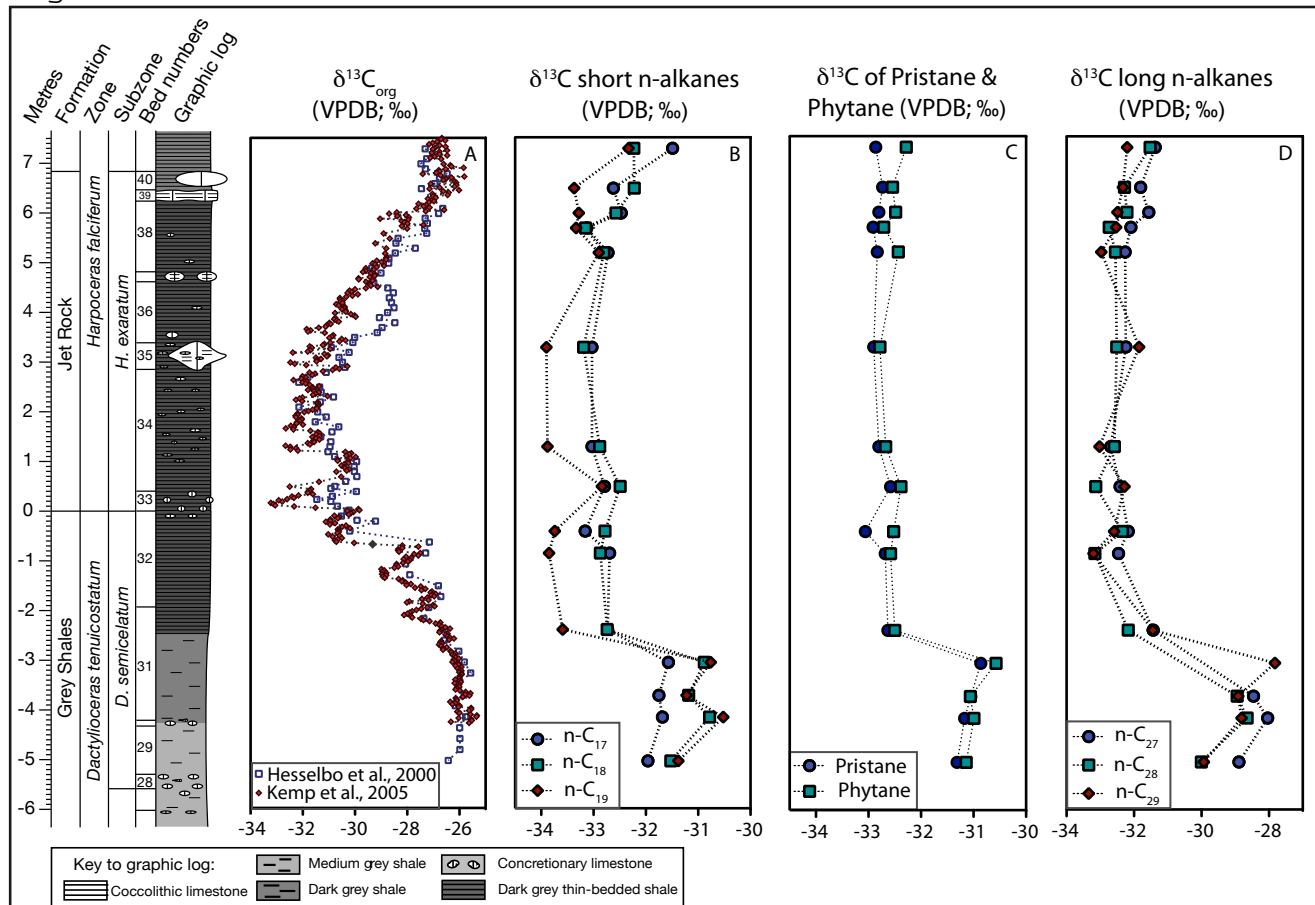


Figure 7



## Supplementary Online Material (SOM)

### *3.1 Rock-Eval pyrolysis*

Powdered sediment samples (~1 g) were analyzed at the University of Newcastle on a Rock-Eval pyrolysis instrument. The total organic carbon (TOC %),  $T_{\max}$  (°C),  $S_1$ , and  $S_2$  were determined. The  $S_1$  and  $S_2$  are expressed in mg hydrocarbons (HC) per gram dry rock. These parameters were used to calculate the hydrogen index (HI) ( $HI = [100 \cdot S_2] / TOC$ ; expressed in mg hydrocarbon (HC)/g TOC) and the production index (PI) ( $PI = S_1 / [S_1 + S_2]$ ). The Rock-Eval TOC values and the bulk  $\delta^{13}C_{org}$  have been previously reported (Hesselbo et al., 2000).

### *3.2 Organic petrography*

In order to examine the nature of the organic matter, particularly the fraction of terrigenous organic matter, four samples across the section were prepared for optical analysis of the kerogen. Kerogen was isolated from the sample material remaining after lipid extraction as described in section 3.3. The mineral matrix was removed by the sequential addition of HCl and HF. Samples were centrifuged and rinsed between acid treatments, and the residual matter was rinsed with water and methanol. A subsample of each kerogen sample was mounted onto a slide in duplicate and assessed optically under white light and fluorescent light using a Zeiss research microscope and a Zeiss x 40 Plan-Neofluar objective. A Zeiss Axioskop, Axio Image D1, and a Zeiss 18 filter set were used to take photomicrographs and fluorescence images.

The fraction of terrigenous organic matter was estimated for the samples that were not analyzed by organic petrography using the linear relationship between the percent terrigenous organic matter measured by optical microscopy and the corresponding HI:

$$f_{Terr\ OM} (\%) = -0.279 * HI + 136 \quad (1)$$

where the linear regression had an  $R^2$  value of 0.90 and  $f_{Terr\ OM}$  represents the terrigenous organic matter as a percentage.

### 3.3 Biomarker extraction and analysis

Powdered samples (~ 5 g) were extracted using a Dionex ASE 200 Accelerated Solvent Extractor at 1000 psi and 100°C, with a solvent mixture of dichloromethane:methanol 9:1 (v/v). The total lipid extract (TLE) was reacted with acid-activated copper shots to remove elemental sulfur. Asphaltenes were separated (3x) from the maltene fraction by precipitation in n-pentane at 4°C, and after centrifugation at 3000 rpm for 10 minutes. The maltene fraction was then separated into saturated, aromatic, and polar fractions by silica gel chromatography using hexane, 1:1 (v/v) hexane/dichloromethane, and 7:3 (v/v) dichloromethane/methanol.

The saturated fractions were screened by gas chromatography-mass spectrometry (GC-MS) in full scan using an Agilent 6890 GC equipped with a HP6890 autosampler and interfaced to an Agilent 5973 mass spectrometer. Saturated hydrocarbons were also analyzed by gas chromatography-metastable reaction monitoring-mass spectrometry (GC-MRM-MS) on a Micromass Autospec Ultima mass spectrometer coupled with an Agilent 6890N GC. The analysis was carried out with a 60 m J&W Scientific DB-1 fused silica capillary column (internal diameter: 0.25 mm; 0.25 m film thickness) in pulsed splitless mode. The initial GC oven temperature was programmed to 60°C (held for 2

minutes), ramped to 150°C at 10°C/minute, and then to 315°C at 3°C/minute (held for 24 minutes). The ion source was in EI mode at a temperature of 250°C, an ionization energy of 70 eV, and acceleration voltage of 8000 kV. Tricyclic terpanes and hopanes were identified by MRM using the molecular ion to the m/z 191 transitions. Likewise, steranes were identified by MRM using the molecular ion to m/z 217 transitions.

The aromatic fraction was analyzed by GC-MS in SIM modes. Prior to analysis, 400 ng of an aromatic internal standard, deuterated phenanthrene, was added to each sample. The GC was fitted with a DB-5 stationary phase column, and the GC oven temperature was ramped from 60°C to 150°C at 20°C/minute, and then to 330°C at 4°C/minute (held for 27 minutes). The aryl isoprenoids and isorenieratane was identified in the m/z 134 ion chromatograms and quantified using the internal standard. Absolute quantification is not possible without taking into account relative response factors but our approach does allow an internally consistent estimation across the sample set.

The aromatic fraction was also analyzed by GC-MS in full scan and MRM modes on a Micromass Autospec Ultima mass spectrometer coupled with an Agilent 6890N GC autospec. The GC was fitted with a DB-5 stationary phase column. Polycyclic aromatic hydrocarbons (PAHs) were identified and quantified in full scan mode by their mass spectra and by comparison with a mix of authentic standards, with the exception of retene, coronene, and triphenylene, which were identified by their mass spectra and relative retention time. Aromatic carotenoid derivatives were also analyzed by GC-MRM-MS using parent-daughter reactions. Isorenieratane, okenane, and chlorobactane were identified in characteristic MRM transitions by comparison of retention times to an extract from the Barney Creek Formation (BCF) and a standard mix of hydrogenated



carotenoids containing chlorobactane, okenane, isorenieratane, renieratane, and renierapurpane. Using the MRM data, okenane and chlorobactane were quantified against the GC-MSD quantified isorenieratane. The aromatic carotenoid derivative and PAH concentrations were normalized against mass of TLE and TOC.

Compound specific carbon isotopic measurements of saturated hydrocarbons were made by gas chromatography/combustion/ isotope ratio mass spectrometry (GC-C-IRMS) using a Thermo Finnigan Delta plus XP coupled to a Thermo Finnigan Trace GC. The initial oven temperature was programmed to 60°C (held for 3 minutes), ramped to 180°C at 10°C/min, and then to 320°C at 4°C/min (held for 20 minutes). All samples were bracketed by pulses of in house calibrated reference CO<sub>2</sub> gas and Oztech calibrated reference CO<sub>2</sub> gas. A standard mix of *n*-alkanes (mix A; Arndt Schimmelmann, Indiana University) was analyzed twice a day to monitor the instrument condition. The mean value of triplicate analyses are reported here in permil (‰) relative to Vienna Pee Dee belemnite (VPDB), and the standard deviation from the mean value was better than 0.4‰.